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Phosphiranes as Ligands: Tungsten(0) and Palladium(0) Complexes of Phosphirano[1,2-c][1,2,3]diazaphospholes

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Phosphirano[1,2-*c*][1,2,3]diazaphospholes **5**, which feature a strongly pyramidalized phosphorus atom at a ring fusion position, were identified as a new type of phosphane ligands for transition metals. The derivatives **5a–c** smoothly form $W(CO)_5$ complexes, which are thermally quite stable – in contrast to the known lability of various carbonylmetal complexes of simple phosphiranes. In the temperature range 120–150 °C, they undergo a clean decomplexation in toluene solution. Bicyclic phosphiranes **5a** and **5b**, but not the acceptor-substituted derivative **5c**, readily react with the [(*E*,*E*)-

dibenzylideneacetone]palladium(0) complex $Pd_2(dba)_3$. CHCl₃ to form the corresponding isolable complexes [(**5a**)₂-(dba)Pd] and [(**5b**)₂(dba)Pd]. In agreement with the formation of these complexes, it was found that **5a,b** as ligands effectively promote the Suzuki cross-coupling of 4-bromotoluene with benzeneboronic acid. The solid-state structure of bicyclic phosphirane **5b** and of the complexes [(**5a**)(CO)₅W], [(**5b**)₂-(dba)Pd] (pentane solvate) and [(**5b**)₂(dba)Pd] (benzene solvate) are determined by X-ray diffraction analysis.

Introduction

Phosphiranes represent a class of phosphorus-containing three-membered heterocycles, the chemistry of which is nowadays widely explored.^[1] In addition to the familiar chemical reactivity of cyclopropanes, which includes onebond ring-opening, [2+1] cycloreversion and ring-expansion processes, the possibility to alter the coordination number and oxidation state of the σ^3 , λ^3 -phosphorus atom characterize the chemical reactivity of the phosphiranes. In the context of coordination chemistry, phosphiranes 1 (Figure 1) can be conceived as a particular subset of phosphane ligands, which differs from common aryl- and/or alkyl-substituted phosphanes in terms of electronic and steric ligand properties. Incorporation of a phosphorus atom in a threemembered ring is connected with a stronger pyramidalization and a change in hybridization, and as a result it is expected that phosphiranes 1 behave as ligands with only weak σ -donor but significant π -acceptor character.^[2–4] On the other hand, a theoretical charge decomposition analysis of platinum complexes of 1-aminophosphirane has revealed that these donor-substituted phosphiranes are relatively good electron donors, but have electron-accepting properties not much different from those of common phosphanes.^[5]

A number of transition-metal complexes containing monocyclic and P,C-fused bicyclic phosphiranes as two-electron donor ligands are known.^[1-4,6-8] Almost all of them

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Figure 1. Selected phosphirane systems as potential ligands in transition-metal complexes.

are of the type $LM(CO)_n$ (L = phosphirane; M = W, Mo, Cr, Fe); [(cod)(1-substituted-2-phenylphosphirane)₂Rh]- $PF_6^{[7]}$ and $cp*IrCl_2(tert-butylphosphirane)^{[2]}$ have to be named as so far rare examples of complexes with transition metals important in contemporary homogeneous catalysis. It may be that the chemical reactivity and limited thermal stability of some phosphiranes and phosphirane complexes prevents a broader application of phosphirane complexes in transition-metal catalysis. As a solution to this problem, Grützmacher and co-workers have developed the so-called BABAR-Phos polycyclic phosphiranes 2.^[3,5,9,10] Formation of isolable complexes with several metals (Cu^I, Rh^I, Pt⁰ and Pt^{II}) has been documented, some of which were found to catalyze efficiently the hydrosilylation (Pt⁰)^[3] and hydroboration (RhI)[10] of olefins. Streubel and co-workers have described the $M(CO)_5$ complexes (M = Mo, W) of several *P*,*C*-cage compounds containing phosphirane subunits.^[11]

Recently we became interested in the suitability of P,Cfused phosphirano-heterophospholes such as 3–5 (Figure 1) as potential ligands for transition metals. Phosphirano-[1,2]thiaphospholes $3^{[12]}$ and $4^{[13]}$ are easily prepared from 1,2-thiaphospholes and diphenyldiazomethane or 9-diazofluorene, respectively, and they smoothly form $W(CO)_5$ complexes. However, these complexes are thermally quite labile. Depending on the individual substitution pattern, the phosphirane ligand in the complex undergoes different isomerization reactions in the temperature range 25-80 °C. When the spiro compounds 4 are heated in acetonitrile solution at 80 °C, decomplexation reconstituting the free phosphirane ligand is the major event. Due to the capricious behavior of 3 and 4 in the ligand sphere of the $W(CO)_5$ complexes, we did not pursue these investigations with other transition metals.

We have now turned our attention to phosphirano[1,2c][1,2,3]diazaphospholes **5**. Compounds of this type were first prepared and investigated by Arbuzov and co-workers during their occupation with the cycloaddition chemistry of 1,2,3-diazaphospholes.^[14] We report now on the chemical and structural characterization of W(CO)₅ and Pd⁰ complexes with bicyclic phosphiranes of type **5** as ligands.

Results and Discussion

Synthesis of Phosphirano-[1,2,3]diazaphospholes 5 and Their Pentacarbonyltungsten Complexes 7

The bicyclic phosphiranes 5a-c are easily obtained in one step from 1,2,3-diazaphospholes 6 and diphenyldiazomethane (Scheme 1). Compounds $5a^{[15]}$ and $5c^{[16]}$ have already been prepared in this manner by Arbuzov and co-workers. We describe here the analogous synthesis of 5b from diazaphosphole 6b, which in turn is readily formed by cyclocondensation of *p*-methoxyacetophenone phenylhydrazone and PCl₃. In addition, since only an IR spectrum of 5a has been published so far, we provide a full characterization by NMR spectroscopy (see Exp. Sect.). The reaction of diphenyldiazomethane with the N-phenyl-substituted diazaphospholes 6a,b is much slower than with the more electron-deficient P=C bond of *N*-acetyl-substituted **6c**. In the case of **6b**, complete conversion required heating at 75 °C for 1 d, and a small excess of the diazo compound was necessary to account for the competing pathways of its thermal decomposition.

On treatment with W(CO)₅(thf), the bicyclic phosphiranes **5a–c** readily form the pentacarbonyltungsten complexes **7a–c**. After chromatographic purification, the latter were obtained in 63–76% yield. These complexes are thermally much more stable than the W(CO)₅ complexes of phosphirano-thiaphospholes **3** and **4** (see Introduction). No isomerization of the bicyclic phosphirane ligand was observed on heating, which corresponds to the thermal stability of the free phosphiranes **5** up to 150 °C (already reported for **5c**^[15]). Only when toluene solutions of **7** were heated in a thick-walled closed Schlenk tube at 120 °C (**7c**) or 150 °C (**7a,b**) for **3** h, clean decomplexation took place,



Scheme 1. Formation of bicyclic phosphiranes **5** and their pentacarbonyltungsten complexes **7**.

which provided after purification the unchanged bicyclic phosphiranes 5 in 72–92% yield.

Table 1 lists significant changes of the NMR spectroscopic data for the phosphirane ring atoms, which occur on complexation of **5a–c**. As it is often observed, the ${}^{31}P$ resonance suffers a shift to lower field, with $\Delta\delta$ values of 42.9, 42.5 and 35.5 ppm, respectively. The ${}^{1}J({}^{31}P, {}^{193}W)$ coupling constant is considered as a good measure for the electronic properties of the ligands; it increases with the electronegativity of the substituents at the phosphorus atom.^[17] The observed values - 287.0 Hz for 5a,b and 296.0 Hz for the somewhat more electron-withdrawing N-acetyl-substituted phosphirane 5c – are a little larger than for Ph_3P – $W(CO)_5$ (280 Hz^[17a]) and at the lower end of the range of (triaminophosphane)W(CO)₅ complexes (290-320 Hz);^[17] furthermore, they are larger by some 10-30 Hz than those of the W(CO)₅ complexes of phosphirano[1,2]thiaphospholes 3 and 4.^[12,13] In (1-phenylphosphirane)W(CO)₅ complexes, values around 260 Hz are typically observed.^[18] Table 1 also shows the characteristic^[1a] diminution of the ${}^{1}J_{\rm PC}$ coupling constants when going from the free to the Pcomplexed phosphirane.

Table 1. Selected NMR spectroscopic data (chemical shifts δ [ppm] and coupling constants J [Hz]) of the phosphirane ring atoms in **5a–c** and their W(CO)₅ complexes **7a–c**.

Compound	δ(C-5)	${}^{1}J_{\rm P,C}(\rm C-5)$	δ(C-6)	${}^{1}J_{P,C}(C-6)$	$\delta(\mathbf{P})$	$^{1}J_{\rm P,W}$
5a	50.3	38.1	32.3	46.8	-75.9	_
7a	44.8	11.0	36.3	19.0	-33.0	287.0
5b	50.4	37.3	32.5	46.8	-76.8	_
7b	44.8	10.2	36.4	19.0	-34.3	287.0
5c	50.4	36.6 ^[a]	38.4	47.6 ^[a]	-92.9	_
7c	44.9	8.8	43.2	21.2	-57.4	296.0

[a] The J(P,C) coupling constants given in ref.^[16b] are not correct.

In order to learn about the structural changes associated with the *P*-complexation of bicyclic phosphiranes **5**, we have determined by X-ray diffraction analysis the structures of phosphirane **5b** and of $5a-W(CO)_5$ in the crystal [suit-

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able crystals of 5b-W(CO)₅ could not be obtained]. Molecule plots are shown in Figures 2 and 3, respectively. In the uncomplexed bicyclic phosphirane 5b, the P-C bond lengths of the phosphirane ring (1.865, 1.878 Å) are within the typical range (1.78-1.89 Å^[1]). The geometrical data for the phosphirane ring match perfectly with those determined for a closely related compound (4-methyl-2,6,6-triphenyl-1phospha-2,3-diazabicyclo[3.1.0]hex-3-ene^[16]). The phosphorus atom is more pyramidalized, as expressed by the sum of bond angles around the phosphorus atom (234.0°), than in the analogous W(CO)₅ complex of phosphiranothiaphosphole 3 (Ar = Ph), where a value of 252.3° was found;^[12] much smaller $\Sigma(PR_3)$ values were reported for phosphirane rings incorporated in a strained cage compound (194.9°^[11a]) or in a dibenzophosphasemibullvalene $(220.1^{\circ[6c]}).$



Figure 2. Molecular structure of bicyclic phosphirane **5b** in the crystal. Selected bond lengths [Å] and angles [°]: P(1)–C(2) 1.865(2), P(1)–C(3) 1.878(2), C(2)–C(3) 1.528(3), P(1)–N(1) 1.737(2); C(2)–P(1)–C(3) 48.19(9), C(2)–C(3)–P(1) 65.44(12), C(3)–C(2)–P(1) 66.37(12), N(1)–P(1)–C(3) 98.54(9), N(1)–P(1)–C(2) 87.29(9). The compound crystallizes from CH₂Cl₂/*n*-pentane with one CH₂Cl₂ molecule in the asymmetric unit. The dichloromethane molecule (not shown here) maintains a hydrogen bond to the methoxy oxygen atom of **5b**, C29–H29A···O1 (–*x*, 1 – *y*, 1 – *z*): C–H 0.99 (H in calculated position), H···O 2.31, C···O 3.227(4) Å, angle C–H···O 154°.

In the $W(CO)_5$ complex of **5a**, the diminution of the electron density at the phosphorus atom leads to a significant shortening of the P–C bonds (1.839, 1.846 Å) and a lengthening of the basal C-C bond (from 1.528 to 1.546 Å) of the three-membered ring. Simultaneously, the pyramidalization at the phosphorus atom is a little reduced, as the sum of bond angles around the phosphorus atom increases from 234.0 to 239.2°. These complexation-induced changes are typical for phosphiranes (see for example, polycyclic phosphiranes $2^{[5]}$ and a closely related dibenzophosphasemibullvalene^[6c]). The complexation by the $W(CO)_5$ fragment also causes a significant conformational change, as the exophenyl substituent at phosphirane ring atom C3 is rotated from the bisecting conformation with respect to the phosphirane ring to an almost perpendicular orientation (the dihedral angle between the cyclopropane ring plane and the



Figure 3. Molecular structure of pentacarbonyltungsten complex **7a** in the crystal. Selected bond lengths [Å] and angles [°]: P–C(2) 1.839(4), P–C(3) 1.846(4), C(2)–C(3) 1.546(5), P–N(1) 1.721(3), W–P 2.4645(10), W–C(29) 2.002(4), W–C(O)_{eq.} 2.036(4) – 2.060(5); C(2)–P–C(3) 49.60(16), C(2)–C(3)–P 64.9(2), C(3)–C(2)–P 65.5(2), N(1)–P–C(3) 100.99(17), N(1)–P–C(2) 88.60(16), C(2)–P–W 127.91 (13), C(29)–W–P 175.29(12).

least-squares plane of the *exo*-phenyl ring is 59.6°). Similar to arylcyclopropanes,^[19] this change is likely to cause, too, small bond-length changes in the three-membered ring. In the octahedrally coordinated P–W(CO)₅ fragment of **7a**, the W–C(O)_{ax} bond (2.002 Å) is shortened compared to the W–C(O)_{eq} bonds due to the *trans* effect of the phosphirane ligand. Interestingly, the W–C(O)_{ax} bond length is virtually the same as in the W(CO)₅ complex of phosphirano-thia-phosphole **3** (Ar = Ph),^[12] and the P–W distances [2.465(1) vs. 2.480(1) Å] are similar.

Palladium(0) Complexes 8

Phosphane ligands play a key role in various palladiumcatalyzed cross-coupling reactions.^[20] In numerous transformations of this kind, a (dba) palladium(0) complex [dba = (E,E)-dibenzylideneacetone] in combination with a trisubstituted phosphane is applied. The coordination equilibria and the role of the dba ligand in these ligand mixtures have been investigated.^[21] One of the first observations was the formation of a heteroleptic Pd⁰ complex according to the equation: $Pd(dba)_2 + 2 PPh_3 \rightarrow (PPh_3)_2(dba)Pd^{[22,23]}$ With (dppe)(dba)Pd [dppe = 1,2-bis(diphenylphosphanyl)ethane], Herrmann and co-workers^[23] presented the first structural characterization of a (benzylideneacetone)diphosphanepalladium(0) complex. Other 16-valence-electron complexes of the type $L_2(dba)Pd^0$ were prepared and structurally characterized subsequently.^[24] To the best of our knowledge, however, the literature holds no report on the use of phosphiranes as ligands in such catalytic reactions nor even on the existence of (phosphirane)palladium(0) complexes.

When the bicyclic phosphiranes 5a,b and $Pd_2(dba)_3$ · CHCl₃ were combined in a molar ratio of 1:4 in [D₁]chloroform, ³¹P NMR spectroscopy showed the clean formation of an AB spin system [e.g. from 5b: $\delta = -30.8$ and -32.0 ppm; $J(P^A, P^B) = 59.2$ Hz]. In contrast, **5c** did not react at all with Pd₂(dba)₃, and the ³¹P NMR spectrum remained unchanged under the same conditions during several days. Obviously, the σ -donating power of N-acetyl-substituted phosphirane 5c is no longer sufficient to ligate with the (dba)Pd complex. In the cases of 5a and 5b, the carriers of the ${}^{31}P{}^{1}H$ NMR signals could be isolated as finely crystalline solids, which started to separate from an acetonitrile solution of the precursors after 15 min. They were identified as the 16-valence-electron complexes [(5a)₂(dba)-Pd] and [(5b)₂(dba)Pd], respectively, by spectroscopic data (NMR, IR) and elemental analyses (Scheme 2). These complexes appear to be stable in the solid state, but their solutions in CDCl₃ show traces of decomposition already after a short time. In the ¹H NMR spectra, broad and little structured signals are observed for the olefinic protons of the Pd-coordinated C=C bond of the dba ligand (the protons of the noncoordinated double bond being superimposed by the aromatic protons) and for the phosphirane proton 5-H as well. The broadening of the dba olefinic proton signals has been noted before by several authors; dynamic NMR studies^[24e,24f] have revealed the existence of several dynamic processes, such as intramolecular interchange between the coordinated and the noncoordinated double bonds, rotational isomerism, and rotation around the Pd-alkene axis.

2 **5a**,**b** + 0.5 Pd₂(dba)₃·CHCl₃



Scheme 2. Complex formation from 5a,b and Pd₂(dba)₃.

The structure of the palladium(0) complexes was confirmed by a crystal structure analysis of [(5b)₂(dba)Pd] (Figure 4). Depending on the conditions of crystallization from benzene/n-pentane, crystals were obtained either as a pentane solvate or a benzene solvate (see Exp. Sect.). In both cases, the crystals have the same space group with similar unit-cell dimensions. As in other [L2(dba)Pd] complexes,^[23,24] the palladium atom has a trigonal-planar coordination geometry with the three ligands. The dba ligand has the s-trans, s-trans conformation at the bonds adjacent to the oxo group, and only one double bond is n-coordinated (Pd-C 2.213 and 2.160 Å). Both the Pd-P distances (2.256 vs. 2.348 Å, mean values) and the P-Pd-P angle (97.6 vs. 112.6°) are distinctly smaller than in a complex with two triarylphosphane ligands, [{[Ph₂(1-naphthyl)]- $P_{2}(dba)Pd$.^[24c] Compared to the bond lengths in the un-



complexed bicyclic phosphirane **5a**, relatively small differences are observed in the two phosphirane rings of the palladium complex: the numerical differences for the C–C bond and the ring-fusing P–C bond are within the sum of the standard deviations, only the P–C(Ph₂) bond is shorter by ca. 0.03 Å. The sum of the N–P–C and C–P–C bond angles is 238.8°, matching very well the value observed for tungsten complex **7a**.



Figure 4. Molecular structure of palladium complex $[(5b)_2(dba)-Pd]$ -0.5 C₅H₁₂ in the crystal. The pentane molecule has been omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–C(2) 1.853(5), P(1)–C(3) 1.847(5), C(2)–C(3) 1.524(5), P(1)–N(1) 1.717(4), P(2)–C(30) 1.857(4), P(2)–C(31) 1.841(5), C(30)–C(31) 1.535(6), P(2)–N(3) 1.712(4), Pd–P(1) 2.2572(13), Pd–P(2) 2.2548(13), Pd–C(57) 2.213(5), Pd–C(58) 2.160(4), C(57)–C(58) 1.389(6), C(59)–O(3) 1.219(6), C(60)–C(61) 1.328(6); C(2)–P(1)–C(3) 48.66(17), C(2)–C(3)–P(1) 65.9(2), C(3)–C(2)–P(1) 65.5(2), N(1)–P(1)–C(3) 101.58(19), N(1)–P(1)–C(2) 88.6(2), C(30)–P(2)–C(31) 49.03(18), C(30)–C(31)–P(2)–6(.0(2), C(31)–C(30)–P(2) 64.9(2), N(3)–P(2)–C(30) 88.4(2), N(3)–P(2)–C(31) 101.41(19), P(1)–Pd–P(2) 97.58(4), C(57)–Pd–C(58) 37.00(16).

Complexes of the type $[(R_3P)_2(dba)Pd]$ are known as precatalysts in the Suzuki cross-coupling reaction leading to biaryls. We have therefore applied ligands 5a-c to the crosscoupling reaction of 4-bromotoluene and benzeneboronic acid to yield 4-methylbiphenyl by using a standard setup (Scheme 3).^[25] The results are shown in Table 2. Bicyclic phosphiranes 5a and 5b are well-suited ligands, whereas the less electron-donating **5c** is little effective, in agreement with its failure to form a stable complex with $Pd_2(dba)_3$ at room temperature (see above). On the other hand, 5a,b are not able to promote the cross-coupling reaction of 4-chlorotoluene with PhB(OH)₂. Assuming that a complex [(phosphirane)₂Pd] is the catalytically active species, a Pd⁰/ligand ratio of 1:2 would be appropriate. A variation of the Pd⁰/5a ratio (Table 2, Entries 2-4) suggests, however, that a ratio less than 2 is more favorable. Fu and co-workers^[25] found a Pd⁰/ $P(tBu)_3$ ratio of 1–1.5 as optimal, and they concluded that the catalytically active palladium species is in fact the monophosphanepalladium complex. Should this also be the case for a palladium complex bearing only one ligand of **5a,b**, one would have to attribute it to the steric demand of these ligands. In terms of their electronic properties, they do not match the much more electron-rich $P(tBu)_3$ ligands.

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Scheme 3. Suzuki cross-coupling reaction. See Table 2 for conditions.

Table 2. Suzuki cross-coupling reaction of 4-bromotoluene and benzeneboronic acid to yield 4-methylbiphenyl: ligand screening.^[a]

Entry	Ligand	Mol-% of Pd^0 vs. ligand	Yield [%]
1	_	1.5, –	16
2	5a	1.5, 3.0	59
3	5a	1.5, 3.6	49
4	5a	1.5, 2.25	95
5	5a	1.5, 1.8	65–73 ^[b]
6	5b	1.5, 3.0	90
7	5c	1.5, 3.0	38

[a] Reagents and conditions: 4-bromotoluene (0.5 mmol), benzeneboronic acid (0.75 mmol), Cs_2CO_3 (1.0 mmol), $[Pd_2(dba)_3]$ · CHCl₃ (1.5 mol-%), ligand **5** (1.5–3 mol-%), 1,4-dioxane (1.5 mL), 80 °C, 48 h. [b] Reaction time: 5 h.

Conclusions

Phosphirano[1,2-c][1,2,3]diazaphospholes 5a,b, representing P,C-fused bicyclic phosphiranes, emerge as a class of potentially useful phosphane ligands. In contrast to the limited thermal stability of several substituted monocyclic phosphiranes and their $M(CO)_n$ complexes, **5a**,**b** and their W(CO)₅ complexes are thermally quite stable – the complexes suffer dissociation only in toluene solution when heated at around 120-150 °C. With [(5a)2(dba)Pd] and [(5b)₂(dba)Pd], the first palladium complexes of any phosphirane could be isolated and structurally characterized. We could show that, in agreement with the formation of these complexes, the catalytic system Pd⁰/5a(b) effectively promotes the Suzuki cross-coupling of 4-bromotoluene with benzeneboronic acid. The unreactivity of 4-chlorotoluene in this coupling reaction is not unexpected, since phosphiranes 5 have to be considered as only modest σ -donors.

Experimental Section

General Information: All reactions were carried out under argon by using standard Schlenk techniques. Rigorously dried solvents were used. Kugelrohr distillations were performed with a Büchi GKR 50 apparatus; oven temperatures are reported. Melting points were measured on samples in open capillaries and are not calibrated. Infrared spectra (IR) were recorded with a Bruker Vector 22 FTIR spectrometer by using KBr pellets. ¹H (400.13 MHz), ¹³C (100.62 MHz) and ³¹P NMR (161.98 MHz) spectra were measured with a Bruker DRX 400 spectrometer. All NMR spectra were recorded in CDCl₃ at 298 K. NMR chemical shifts were referenced to the solvent peak for ¹H (CHCl₃: δ = 7.26 ppm) and ¹³C (CDCl₃:

 δ = 77.00 ppm) NMR spectra, and to external 85% H₃PO₄ for ³¹P NMR spectra. If necessary, signal assignments were based on COSY, HMBC, and HSQC experiments. Mass spectra in the chemical ionization mode (CI) were recorded with a Finnigan MAT SSQ 7000 spectrometer.

Starting Materials: Diphenyldiazomethane^[26] was prepared by dehydrogenation of the corresponding hydrazone using a sixfold excess of activated MnO₂. *p*-Methoxyacetophenone phenylhydrazone,^[27] and 1-(4-methyl-6,6-diphenyl-2,3-diaza-1-phosphabicy-clo[3.1.0]hex-3-en-2-yl)ethanone (**5c**)^[16] were prepared by published procedures.

4-(4-Methoxyphenyl)-2-phenyl-2H-1,2,3-diazaphosphole (6b): PCl₃ (4.00 mL, 45.7 mmol) was added carefully to a solution of p-methoxyacetophenone phenylhydrazone (11.0 g, 45.7 mmol) in toluene (100 mL), and the reaction mixture was heated at reflux for 48 h. Addition of triethylamine (7.62 mL, 55.0 mmol) to the slightly yellow solution led to a voluminous precipitate, which was filtered off. The filtrate was stirred with silica gel (5 g) for 5 min. After removal of the silica gel, the filtrate was kept at -35 °C for 2 d to precipitate 6b. Further purification was achieved by Kugelrohr distillation $(1.5 \times 10^{-4} \text{ mbar/160 °C})$. The product was obtained as a colorless solid (8.95 g, 73%), m.p. 99 °C. IR (KBr): $\tilde{v} = 1608$ (s), 1592 (s), 1523 (s), 1507 (m), 1490 (s), 1453 (m), 1438 (s), 1418 (s), 1363 (m), 1300 (m), 1287 (s), 1234 (s), 1176 (s), 1028 (s), 836 (s), 772 (s), 752 (s) cm⁻¹. ¹H NMR: δ = 3.87 (s, 3 H, CH₃), 7.00 (d, ³J_{H,H} = 8.8 Hz, 2 H, H_{Ph}), 7.31 (m, 1 H, H_{Ph}), 7.45 (m, 2 H, H_{Ph}), 7.89 (m, 4 H, H_{Ph}), 8.18 (d, ${}^{2}J_{PH}$ = 44.7 Hz, 1 H, 3-H) ppm. ${}^{13}C{}^{1}H$ NMR: δ = 55.3 (s, CH₃), 113.1, 113.6, 114.1, 119.9, 120.1, 126.8, 127.8, 129.2, 129.3, 134.2, 134.5 (d, ${}^{2}J_{P,C}$ = 8.8 Hz, C-5), 158.7 (d, ${}^{1}J_{P,C}$ = 36.6 Hz, C-4), 159.9 ppm. ³¹P NMR: δ = 229.2 ppm. MS (CI = 100 eV): m/z (%) = 269 (100) [MH]⁺, 268 (50) [M]⁺. C₁₅H₁₃N₂OP (268.3): calcd. C 67.16, H 4.88, N 10.44; found C 67.13, H 5.13, N 10.17.

2,4,6,6-Tetraphenyl-2,3-diaza-1-phosphabicyclo[3.1.0]hex-3-ene (5a): Prepared as described below for **5b**, from 2,5-diphenyl-2*H*-1,2,3-diazaphosphole and diphenyldiazomethane. Pale yellow solid, m.p. 138 °C. ¹H NMR: δ = 4.57 (d, ²*J*_{P,H} = 19.5 Hz, 1 H, 5-H), 6.89 (m, 2 H, H_{Ph}), 6.98 (t, ³*J*_{H,H} = 7.3 Hz, 1 H, H_{Ph}), 7.10–7.46 (m, 14 H, H_{Ph}), 7.90 (dd, ³*J*_{H,H} = 8.2, 1.4 Hz, 2 H, H_{Ph}) ppm. ¹³C{¹H} NMR: δ = 32.3 (d, ¹*J*_{P,C} = 46.8 Hz), 50.3 (d, ¹*J*_{C,P} = 38.1 Hz), 116.2 (d, *J*_{P,C} = 10.2 Hz), 122.0, 125.6, 125.7, 126.7, 127.6, 128.5, 128.6, 128.8, 129.1, 132.1, 134.4, 134.9, 143.9 (d, *J*_{P,C} = 15.4 Hz), 145.0 (d, *J*_{P,C} = 13.2 Hz), 151.1 ppm. ³¹P NMR: δ = -75.9 ppm.

4-(4-Methoxyphenyl)-2,6,6-triphenyl-2,3-diaza-1-phosphabicyclo-[3.1.0]hex-3-ene (5b): A solution of 6b (2.66 g, 9.91 mmol) and diphenyldiazomethane (2.30 g, 11.8 mmol) in toluene (90 mL) was heated at 75 °C, until the red color of the diazo compound had disappeared (24 h). The solvent was partly removed in vacuo, subsequent addition of methanol led to the precipitation of the product. Recrystallization from dichloromethane/n-pentane gave 5b as yellow crystals (3.42 g, 80%) containing 1 equiv. of CH₂Cl₂, which can be removed in vacuo; m.p. (after drying) 131 °C. IR (KBr): v = 1594 (s), 1512 (m), 1493 (s), 1443 (m), 1365 (m), 1306 (s), 1257 (s), 1176 (s), 751 (s), 699 (s) cm⁻¹. ¹H NMR: δ = 3.87 (s, 3 H, CH₃), 4.51 (d, ${}^{2}J_{PH}$ = 19.2 Hz, 1 H, 5-H), 6.87 (d, ${}^{3}J_{H,H}$ = 7.6 Hz, 2 H, H_{Ph}), 6.94 (d, ${}^{3}J_{H,H}$ = 8.8 Hz, 2 H, H_{Ph}), 6.96 (t, ${}^{3}J_{H,H}$ = 8.8 Hz, 1 H, H_{Ph}), 7.11 (m, 3 H, H_{Ph}), 7.16 (m, 3 H, H_{Ph}), 7.27 (m, 4 H, H_{Ph}), 7.44 (d, ${}^{3}J_{H,H}$ = 8.1 Hz, 2 H, H_{Ph}), 7.84 (d, ${}^{3}J_{H,H}$ = 8.6 Hz, 2 H, H_{Ph}) ppm. ¹³C NMR: δ = 32.5 (d, ¹J_{P,C} = 46.8 Hz, C-6), 50.4 (d, ${}^{1}J_{P,C}$ = 37.3 Hz, C-5), 55.3 (s, CH₃), 114.0, 116.0, 121.7, 125.3, 125.6, 127.3, 127.5, 128.2, 128.5, 129.0, 132.1, 134.9, 137.9, 144.1 (d, ${}^{2}J_{P,C}$ = 14.6 Hz, C-4), 145.1, 151.2, 160.3 ppm. ${}^{31}P{}^{1}H$ NMR:



 δ = -76.8 ppm. MS (CI = 100 eV): *m/z* = 435 [MH]⁺. C₂₈H₂₃N₂OP (434.5) + 1.0 CH₂Cl₂: calcd. C 67.06, H 4.85, N 5.39; found C 67.14, H 4.83, N 5.38.

Pentacarbonyltungsten Complexes 7a–c. General Procedure: A solution of hexacarbonyltungsten (1.83 mmol) in tetrahydrofuran (200 mL) was placed in a photolysis apparatus and irradiated by using a 150 W medium-pressure mercury lamp for 60 min. The yellow solution of the formed complex $W(CO)_5$ (thf) was transferred through a cannula to a flask containing the solid phosphirane **5** (1.60 mmol), and the mixture was stirred for 1 d. The solvent was removed in vacuo, and the resulting oil was purified by column chromatography on silica gel with toluene/cyclohexane (1:1) as eluent.

Pentacarbonyl(2,4,6,6-tetraphenyl-2,3-diaza-1-phosphabicyclo-[3.1.0]hex-3-ene-*kP*)tungsten (7a): Synthesis according to the General Procedure from W(CO)₆ (0.640 g, 1.83 mmol) and **5a** (0.650 g, 1.60 mmol). Recrystallization from toluene gave 7a as yellow crystalline plates (0.730 g, 63%); m.p. 195 °C. IR (KBr): $\tilde{v} = 2079$ (vs), 1995 (s), 1938 (vs, br.), 1596 (m), 1491 (s), 1445 (m), 1360 (m), 1277 (m), 756 (s), 693 (s), 592 (s), 568 (s) cm⁻¹. ¹H NMR: δ = 4.90 (d, ${}^{2}J_{\rm P,H}$ = 3.5 Hz, 1 H, 5-H), 7.10–7.56 (m, 18 H, H_{Ph}), 7.96 (d, ${}^{3}J_{\rm H,H}$ = 6.8 Hz, 2 H, H_{Ph}) ppm. ¹³C{¹H} NMR: δ = 36.3 (d, ¹J_{PC} = 19.0 Hz, C-6), 44.8 (d, ${}^{1}J_{PC} = 11.0$ Hz, C-5), 122.0, 125.0, 126.6, 127.7, 127.9, 128.6, 128.7, 128.8, 129.0, 129.3, 129.3, 130.9, 133.8, 136.0, 138.6, 141.2, 150.9, 193.8 (d, ${}^{2}J_{P,C} = 8.1 \text{ Hz}, \text{ CO}_{eq}$), 196.5 (d, ${}^{2}J_{PC} = 40.3 \text{ Hz}$, CO_{ax}) ppm. ${}^{31}P{}^{1}H$ NMR: $\delta = -33.0 ({}^{1}J_{PW} =$ 287.0 Hz) ppm. MS (CI = 100 eV): m/z (%) = 728 (28) [M]⁺, 405 (100) $[M - W(CO)_5 + 1]^+$. $C_{32}H_{21}N_2O_5PW$ (728.4): calcd. C 52.77, H 2.91, N 3.85; found C 53.06, H 3.00, N 3.71.

Pentacarbonyl{4-(4-methoxyphenyl)-2,6,6-triphenyl-2,3-diaza-1phosphabicyclo[3.1.0]hex-3-ene-kP}tungsten (7b): Synthesis according to the General Procedure from W(CO)₆ (0.640 g, 1.83 mmol) and **5b** (0.700 g, 1.60 mmol). Yellow solid (0.870 g, 72%); m.p. 190 °C. IR (KBr): $\tilde{v} = 2080$ (vs), 1996 (s), 1941 (vs, br.), 1607 (m), 1596 (m), 1513 (m), 1491 (m), 1446 (m), 1361 (s), 1306 (m), 1257 (s), 1176 (m), 1025 (m), 701 (s), 693 (s), 589 (s), 571 (s) cm⁻¹. ¹H NMR: δ = 3.90 (s, 3 H, CH₃), 4.89 (d, ²J_{PH} = 4.9 Hz, 1 H, 5-H), 7.03 (d, ${}^{3}J_{H,H}$ = 8.8 Hz, 2 H, H_{Ph}), 7.13–7.43 (m, 13 H, H_{Ph}), 7.53 (d, ${}^{3}J_{H,H}$ = 8.1 Hz, 2 H, H_{Ph}), 7.93 (d, ${}^{3}J_{H,H}$ = 8.6 Hz, 2 H, H_{Ph}) ppm. ¹³C{¹H} NMR: δ = 36.4 (d, ¹J_{P,C} = 19.0 Hz, C-6), 44.8 (d, ${}^{2}J_{P,C}$ = 10.2 Hz, C-5), 55.4 (s, CH₃), 114.2, 121.9, 124.7, 125.3, 126.5, 127.6, 127.9, 128.6, 129.0, 129.2, 130.8, 135.9, 137.9, 138.7, 141.3, 150.8, 160.7, 193.9 (d, ${}^{2}J_{PC}$ = 8.1 Hz, CO_{ea}), 196.5 (d, ${}^{2}J_{PC}$ = 40.0 Hz, CO_{ax}) ppm. ³¹P NMR: δ = -34.3 (¹J_{PW} = 287.0 Hz) ppm. MS (CI = 100 eV): m/z (%) = 758 (13) [M]⁺, 435 (38) [M -W(CO)₅]⁺. C₃₃H₂₃N₂O₆PW (758.4): calcd. C 52.26, H 3.06, N 3.69; found C 52.43, H 3.16, N 3.86.

Pentacarbonyl{1-(4-methyl-6,6-diphenyl-2,3-diaza-1-phosphabicyclo-[3.1.0]hex-3-en-2-yl)ethanone-κ*P*}tungsten (7c): Synthesis according to the General Procedure from W(CO)₆ (0.640 g, 1.83 mmol) and 5c (0.490 g, 1.60 mmol). Yellow solid (0.770 g, 76%); m.p. 140 °C. IR (KBr): $\tilde{v} = 2081$ (s), 1969 (vs), 1949 (vs, br.), 1671 (s), 1447 (m), 1387 (m), 1337 (m), 757 (m), 706 (m), 693 (m), 571 (s) cm^{-1.} ¹H NMR: $\delta = 2.01$ (s, 3 H, CH₃), 2.25 (s, 3 H, CH₃), 3.98 (d, ²*J*_{P,H} = 6.3 Hz, 1 H, 5-H), 7.13–7.38 (m, 10 H, H_{Ph}) ppm. ¹³C{¹H} NMR: $\delta = 19.4$ (d, ³*J*_{P,C} = 2.2 Hz, CH₃), 22.1 (s, CH₃), 43.2 (d, ¹*J*_{P,C} = 21.2 Hz, C-6), 44.9 (d, ¹*J*_{P,C} = 8.8 Hz, C-5), 128.0, 128.2, 128.5, 128.6, 128.9, 129.3, 130.7, 136.1, 137.3, 156.1 (d, ²*J*_{P,C} = 2.9 Hz, C-4), 173.9 (d, ²*J*_{P,C} = 7.3 Hz, CH₃CO), 194.0 (d, ²*J*_{P,C} = 8.0 Hz, CO_{eq}), 197.1 (d, ²*J*_{P,C} = 43.9 Hz, CO_{ax}) ppm. ³¹P{¹H} NMR: $\delta =$ -57.4 (¹*J*_{P,W} = 296.0 Hz) ppm. MS (CI = 100 eV): *m*/z (%) = 633 (100) [MH]⁺, 604 (61) [M - CO]⁺, 577 (10) [M - 2 CO]⁺, 549 (4) $[M - 3 CO]^+$, 494 (5) $[M - 5 CO]^+$, 309 (53) $[M - W(CO)_5]^+$. C₂₃H₁₇N₂O₆PW (632.2): calcd. C 43.70, H 2.71, N 4.43; found C 43.89, H 2.81, N 4.37.

Decomplexation of Complexes 7a–c: A solution of the complex (0.130 mmol) in toluene (10 mL) was placed in a sealed tube and heated at 120 °C (**7c**) or 150 °C (**7a,b**) for 3 h. The solvent was removed in vacuo. For further purification, a solution of the residue in toluene/cyclohexane (1:1) was passed through a short pad of silica gel (5 g). Evaporation of the solvent furnished phosphiranes **5a** [72% yield; m.p. 138 °C (dec.)], **5b** [77% yield; m.p. 131 °C (dec.)], and **5c** [92% yield; m.p. 136 °C (dec.); ref.^[16b] 132–135 °C], respectively.

[(5a)₂(dba)Pd]: Pd₂(dba)₃·CHCl₃ (12.9 mg, 12.5 µmol) and bicyclic phosphirane **5a** (20.2 mg, 50 µmol) were placed in a Schlenk tube and dissolved in dry acetonitrile (1 mL). Separation of a finely crystalline lemon-colored precipitate started after 15 min. Stirring was continued for another 75 min, and the yellow solid was isolated by centrifugation in virtually quantitative yield. ¹H NMR (complex·CH₃CN): $\delta = 2.00$ (s, 3 H, CH₃CN), 3.01 (br. d, 2 H, phosphirane-H), 4.92 (br., 1 H, CH_{olefin} dba), 5.42 (br., 1 H, CH_{olefin} dba), 6.22 (d, 1 H), 6.42–7.85 (all H_{aryl} and CH=CH dba) ppm. ³¹P{¹H} NMR: $\delta = -30.3$ and -31.4 (AB system, $J_{P,P} = 60.4$ Hz) ppm. $C_{71}H_{56}N_4OP_2Pd$ ·CH₃CN (1149.61 + 41.05): calcd. C 73.64, H 4.99, N 5.88; found C 73.95, H 5.06, N 5.36.

[(5b)₂(dba)Pd]: Preparation as described above, but from **5b** (28.6 mg, 65.7 μmol) and 15.1 μg (14.5 mmol) of Pd₂(dba)₃·CHCl₃. Yield: 34.6 mg (98%). IR (KBr): $\tilde{v} = 1560$ (m, C=O), 1596 (s), 1489 (s), 760 (s), 696 (s) cm⁻¹. ¹H NMR (complex·CH₃CN): $\delta = 2.00$ (s, 3 H, CH₃CN), 3.02 (br., 2 H, H phosphirane), 3.88 (s, 6 H, OCH₃), 4.91 (br., 1 H, CH_{olefin} dba), 5.38 (br., 1 H, CH_{olefin} dba), 6.20 (d, 1 H), 6.41–7.85 (all H_{aryl} and CH=CH dba) ppm. ³¹P{¹H} NMR: $\delta = -30.8$ and -32.0 (AB system, $J_{P,P} = 59.2$ Hz) ppm. C₇₃H₆₀N₄O₃P₂Pd·CH₃CN (1209.67 + 41.05): calcd. C 73.64, H 4.99, N 5.88; found C 73.95, H 5.06, N 5.36. Crystals used for X-ray structure determination: C₇₃H₆₀N₄O₃P₂Pd·C₅H₁₂ (1209.67 + 72.15): calcd. C 73.09, H 5.66, N 4.37; found C 73.39, H 5.32, N 4.34.

Suzuki Cross-Coupling Reactions: The ligand 5a–c (3 mol-%), benzeneboronic acid (0.75 mmol), Cs_2CO_3 (1.00 mmol) and $[Pd_2-(dba)_3]$ ·CHCl₃ (1.5 mol-%) were placed in a vial that could be closed with a screw-cap. After addition of 4-bromotoluene (0.50 mmol) and degassed 1,4-dioxane (1.5 mL) under an inert gas, the reaction mixture was heated in a heating block at 80 °C. After 48 h, the reaction was stopped and the product ratio determined. For this purpose, an aliquot was withdrawn from the reaction mixture and analyzed unchanged (i.e. without evaporation of volatiles) by NMR spectroscopy. The quoted yields are average yields obtained from 2–4 independent runs.

Crystal Structure Determinations: Data collection was performed with an image-plate diffractometer (Stoe IPDS) by using monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by using a full-matrix leastsquares method. Hydrogen-atom positions were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. For **5b** and **7a**, the phosphirane ring proton was localized in a ΔF map and refined isotropically. Software for structure solution and refinement: SHELX-97;^[28] molecule plots: OR-TEP-3.^[29] Further details are provided in Table 3. **5b:** Crystals of **5b·**CH₂Cl₂ were obtained by crystallization from a dichloromethane/*n*-pentane solution. The occupancy factor of the CH₂Cl₂ molecule was refined to be 0.974(3). **7a:** Suitable crystals were obtained by slow concentration of a diethyl ether solution. **[(5b)₂(dba)Pd]:** A

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Table 3. Crystallographic data and details of data collection and structure refinement for **5b**, **7a** and $[(5b)_2(dba)Pd]$ (pentane solvate and benzene solvate).^[a]

	5b	7a	[(5b) ₂ (dba)Pd] Pentane solvate	Benzene solvate
			Tentane solvate	Delizene solvate
Empirical formula	$C_{28}H_{23}N_2OP \cdot CH_2Cl_2$	$C_{32}H_{21}N_2O_5PW$	$C_{73}H_{60}N_4O_3P_2Pd\cdot 0.5C_5H_{12}$	$C_{73}H_{60}N_4O_3P_2Pd\cdot C_6H_6$
Formula mass	519.38	728.33	1209.67 + 36.07	1209.67 + 78.11
Temperature [K]	193(2)	193(2)	193(2)	193(2)
Crystal size [mm]	$0.38 \times 0.27 \times 0.12$	$0.46 \times 0.27 \times 0.12$	$0.27 \times 0.15 \times 0.04$	$0.31 \times 0.15 \times 0.08$
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P 2_1/n$	$P 2_1/n$	$P 2_1/n$
<i>a</i> [Å]	10.6055(16)	10.2133(12)	12.6691(15)	11.0142(13)
<i>b</i> [Å]	11.2442(16)	12.0170(10)	23.2646(19)	27.1081(19)
c [Å]	12.0606(17)	23.598(3)	21.120(2)	21.942(3)
	63.898(15)	90	90	90
β [°]	86.271(18)	96.389(15)	99.355(13)	100.974(14)
γ [°]	86.892(18)	90	90	90
Volume [Å ³]	1288.3(3)	2878.3(5)	6142.2(11)	6431.5(12)
Ζ	2	4	4	4
Density [g cm ⁻³]	1.339	1.681	1.347	1.330
$\mu(\text{Mo-}K_{\alpha}) \text{ [mm^{-1}]}$	0.34	4.113	0.408	0.392
F (000)	540	1424	2588	2672
θ range [°]	2.07-25.02	2.10-25.98	2.14-25.03	2.03-25.95
Reflections collected	14588	10205	44282	47861
Independent reflections (R_{int})	4298 (0.0483)	5429 (0.0264)	10527 (0.1420)	12009 (0.2079)
Completeness to θ_{max} [%]	94.3	96.0	97.0	95.5
Absorption correction	_	numerical	_	_
Max/min transmission	_	0.5676/0.3320	_	_
Data/restraints/parameters ^[b]	4298/0/322	5429/0/374	10527/0/778	12009/0/804
Goodness-of-fit on F^2	0.923	0.991	0.758	0.812
Final R indices $[I > 2\sigma(I)]$: R_1 , $wR_2^{[b]}$	0.0398, 0.0905	0.0230, 0.0531	0.0446, 0.0633	0.0719, 0.0746
R indices (all data): R_1 , $wR_2^{[c]}$	0.0682, 0.0978	0.0309, 0.0635	0.1226, 0.0780	0.1460, 0.0906
Largest diff. peak, hole [e Å-3]	0.52, -0.39	0.71, -1.15	0.48, -0.83	0.64, -0.59

[a] CCDC-760810 (for **5b**), -760809 (for **7a**), -760811 {for [(**5b**)₂(dba)Pd] (pentane solvate)}, and -760812 {for [(**5b**)₂(dba)Pd] (benzene solvate)} contain the supplementary crystallographic data for this paper, These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [b] Refinement based on F^2 values. [c] $R_1 = \Sigma ||F_0| - |F_c|/\Sigma ||F_0|$; $wR_2 = {\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2}^{1/2}$.

benzene solution of the complex was exposed to pentane vapors in a closed vessel. At room temperature, crystals were formed as a pentane solvate (C₇₃H₆₀N₄O₃P₂Pd·C₅H₁₂), but crystallization at 5 °C furnished crystals containing one benzene molecule per asymmetric unit $(C_{73}H_{60}N_4O_3P_2Pd\cdot C_6H_6)$. In the crystal structure of the former complex, the pentane molecules are positionally disordered: The midpoint of the C3-C4 bond of the pentane molecule coincides with a crystallographic inversion center, so that an *n*-hexane molecule is simulated. However, when the molecule was refined as an *n*-hexane molecule, the temperature factors of the methyl carbon atom became unusually high. The disorder was not fully taken into account in the refinement (the 2-methylene group in one pentane molecule coincides with the terminal CH₃ group of the pentane in the inversion-related position). For the crystal structure of the benzene solvate complex, large and strongly anisotropic amplitudes of thermal vibration were found, but no efforts were made to introduce any constraints in the refinement procedure.

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